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Measurement of Dry Deposition and Air−Water Exchange of Polycyclic Aromatic Hydrocarbons with the Water Surface Sampler

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Recent work has shown that dry deposition and gas exchange of semivolatile organic compounds in the Great Lakes is important. However, there is no generally accepted method for collecting particulate dry deposition or gas exchange. In this work the Water Surface Sampler (WSS) was modified and used in combination with dry deposition plates to measure the particulate dry deposition and gas exchange of PAHs. Simultaneous dry deposition and ambient air samples were collected between June and October 1995 in Chicago, IL. Total (particulate + gas) fluxes were measured with the WSS, while particulate fluxes were measured with dry deposition plates. Average Σ_{14}-PAH and particulate Σ_{14}-PAH fluxes were 360 ± 146 μg/m^2 d and 144 ± 60 μg/m^2 d, respectively. Gas-phase fluxes, determined by subtracting the dry deposition plate fluxes (particulate) from WSS fluxes (particulate + gas), averaged 170 ± 72 μg/m^2 d. The measured particulate dry deposition and gas exchange fluxes were substantially higher than those previously reported for the Great Lakes and nonurban areas, probably due to the significantly higher ambient PAH concentrations found in Chicago. Particulate phase overall dry deposition velocities calculated using the dry deposition fluxes and ambient concentrations averaged 6.7 ± 2.8 cm/s. This value is higher than values estimated using dry deposition models; however, it is in good agreement with values determined using similar techniques.

Introduction

Dry deposition is the transfer of airborne gases and particles to the earth's surface, including soil, water, and vegetation, where they are removed (*1*). The removal rate by dry deposition is a function of the physical and chemical properties of the pollutant, meteorological conditions (temperature, wind speed, atmospheric stability), and surface characteristics. Since the mid-1980s it has been commonly accepted that the impact of atmospheric deposition of semivolatile organic compounds (SOCs) to the Great Lakes is large (*2*). Historically, most efforts to determine the loadings of SOCs have monitored the concentrations of these compounds in precipitation (*3*). Mass balance approaches (*4*) and application of paired or unpaired air and water concentration measurements with the two-film model have also been used to estimate atmospheric loadings of SOCs to the lakes (*2, 5*−*7*).

Current dry deposition estimation methods often use measured air concentrations and modeled dry deposition velocities. These models assume the dry deposition flux of particles (F_p) can be estimated by using an overall particle dry deposition velocity (V_p) and particle phase air concentration (C_p):

$$F_p = V_p \cdot C_p \tag{1}$$

To date there has been no consensus on the appropriate dry deposition velocity to use in these types of models. Estimated (*2*) and experimental (*8*) dry deposition velocities of SOCs range over an order of magnitude.

One of the reasons for this discrepancy is that deposition velocity is a function of particle size. Gravitational settling has a significant effect on the deposition of coarse particles, while Brownian motion dominates the deposition of very fine particles (<0.1 μm) (*1*). As the particle diameter increases the magnitude of flux increases due to higher deposition velocities. A recent study has shown that a multistep modeling approach, which divides the fine and coarse particle distributions into a number of intervals and assigns an appropriate deposition velocity to each interval, gives a better estimate of dry deposition than the approach shown in eq 1 (*9*). Using this multistep model and other techniques it has been found that coarse particles (>2.5 μm) and compounds associated with them are responsible for the majority of dry deposition (*9*−*11*).

There have also been many efforts to measure dry deposition directly. However, there is no generally accepted method for collecting particulate dry deposition or gas exchange. Different kinds of surrogate surfaces including Teflon plates, Petri dishes, dry or diol-coated filters, buckets, pans filled with water, oil-coated glass plates, and greased strips have all been used to measure particle dry deposition (*12*). Recently, using a water surface sampler (WSS) in combination with a greased surrogate surface, Yi (*13*) was able to measure both the gas-phase SO_2 and particulate sulfate flux.

The objectives of this study were to measure the air−water exchange and particulate dry deposition of polycyclic aromatic hydrocarbons (PAHs) and characterize the collection properties of the WSS. In this paper, we report PAH fluxes measured at Chicago, IL in 1995 and compare the particle collection properties of the WSS and dry deposition plates.

Experimental Section

Sample Collection. Twelve dry deposition and ambient air samples were collected between June and October 1995. All samples were collected during the daytime when there was no rain. Average sampling time was 6 days (6 × 12 h) for dry deposition samples and 24 h (2 × 12 h) for air samples (3/dry deposition sample). The average sampling volume for air samples was about 140 m^3.

Samples were taken on a 1.6 m-high platform on the roof of a four-story building (12 m height) located on the campus

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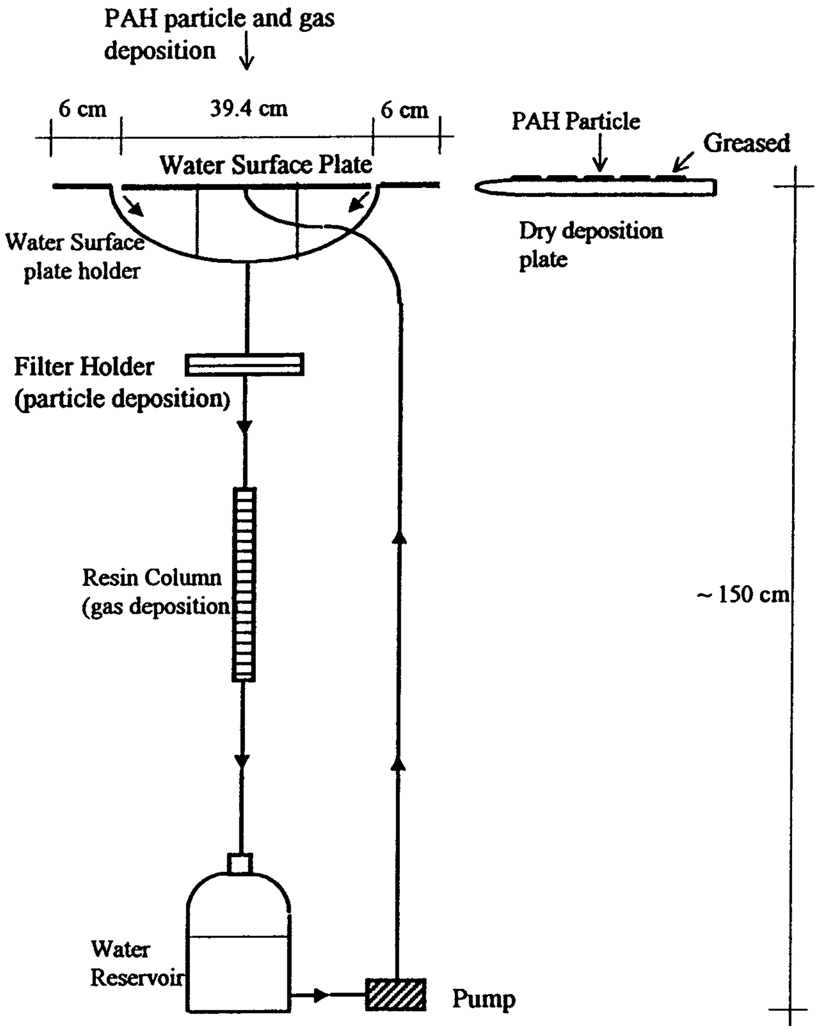

FIGURE 1. Water surface sampler (WSS1) and dry deposition plate used to measure total (particle + gas) and particle PAH dry deposition.

of Illinois Institute of Technology, 5.6 km south of Chicago's center and 1.6 km west of Lake Michigan. The sampling site is in a mixed institutional, residential, commercial area and is the urban research and monitoring site of the Integrated Atmospheric Deposition Network (IADN). There are landscaped areas, large parking lots, and low-rise buildings around the sampling site (*14*).

Water Surface Sampler (WSS). Total (particulate + gas) PAH fluxes were measured using an aerodynamically smooth, circular, water collection surface similar to the one used by Yi (*13*); however, the WSSs used in this study contained a filter (WSS1 only) and a resin column in the water recirculation system and were made of aluminum and stainless steel.

The water surface holder has an airfoil shape with a sharp leading edge to minimize airflow disruptions caused by collector geometry (Figure 1). The water surface plate (39.4 cm diameter, 0.65 cm depth) was made of aluminum. It is placed inside the holder at a height which allows the water on the plate to be at the same level as the top of the water surface holder.

The WSS has a water replenishing system to maintain a constant water level and control the water retention time on the surface. Water enters the water surface plate from its center and overflows from the triangular weirs located at the sides. The retention time on the water surface is maintained as short as possible (2−4 min) in order to prevent losses of deposited PAHs. The recycled water goes through a filter which collects particles (WSS1 only) and a resin (XAD-2) column which adsorbs dissolved PAHs before completing a cycle.

All tubings and fittings were made of Teflon or stainless steel to minimize adsorption. A 4-L aspirator bottle was used as the water reservoir. The pump was a chemical-resistant (all wetted parts were made of Teflon) adjustable liquid pump.

Dry Deposition Plate. The particulate phase dry deposition flux was measured using a smooth greased plate with a sharp leading edge (<10°), mounted on a wind vane. This type of deposition plate was used successfully as a surrogate surface by others to directly measure particulate dry deposition (*8, 10, 13*). The dimensions of the each greased strip were 5.7 × 1.8 cm. Five plates and 20 strips with a total collection area of 205.2 cm^2 were used.

PS-1 Sampler. Air samples were collected by using a modified high-volume sampler Model PS-1 (General Metal Works Inc.). Particles were collected on 11 cm diameter glass fiber filters. The gas-phase compounds were collected in a modified cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF).

Sample Preparation. NaCl and Na_2SO_4 placed in beakers and glass fiber filters were wrapped loosely with aluminum foil and baked in a muffle furnace at 450 °C overnight. Then they were allowed to cool to room temperature in a desiccator (*15, 16*).

PUF Cartridges and XAD-2 resin used in the WSS adsorbent column were cleaned by Soxhlet extraction using a series of solvents (deionized water, methanol, dichloromethane, acetone-hexane mixture) for 24 h each. After extraction, cartridges and resin were wrapped loosely with aluminum foil and dried in an oven at 70 °C. Cleaned resin and cartridges were stored in glass jars capped with Teflon-lined lids (*6, 16*).

Mylar was cut into strips (7.6 × 2.5 cm), and the area to be greased (5.7 × 1.8 cm) was marked with a mechanical pen. Then the strips were rinsed with methanol and deionized (DI) water. Cleaned Mylar strips were coated with ~1.5 mg of Apezion type L grease. Strips were mounted on dry deposition plates, and ungreased areas were covered with PVC covers to prevent exposure to the deposited material during field sampling (*8, 10, 13, 17*).

All wetted components of the WSS were rinsed with deionized (DI) water, methanol, dichloromethane, acetone, and hexane prior to sampling.

Cleaned and prepared glass fiber filters, PUF cartridges, WSS resin columns, and dry deposition plates were transported to the field in their containers without allowing exposure to ambient air. After sampling WSS and PS-1 filters, PUF cartridges and plates were placed back into their containers. The samples were brought back to the laboratory and stored in the dark at 0 °C until they were analyzed.

Air filters, sorbent cartridges, and greased strips were Soxhlet extracted with a mixture of dichloromethane (DCM): petroleum ether (PE) (20:80) for 24 h. The WSS samples (filter and resin) were Soxhlet extracted with methanol (MeOH) followed by DCM for 24 h. PAHs in the MeOH extract were back-extracted three times using equivalent amounts (as volume of MeOH fraction) of saturated NaCl solution and deionized (DI) water and 50 mL of DCM and then combined with the DCM fraction of the same WSS sample. After back-extraction, the DCM fraction was extracted with DI water to remove any residual MeOH. The DCM fraction was then drained through a glass column containing 25 g of clean anhydrous Na_2SO_4 to remove any residual water (*16*).

All sample extracts were concentrated and transferred into hexane using a rotary evaporator and a high purity stream of nitrogen. After volume reduction to 2 mL and transfer into hexane, samples were cleaned on an alumina-silicic acid column containing 3 g of silicic acid (3% water) and 2 g of alumina (6% water). The column was prewashed with 20 mL of DCM followed by 20 mL of PE. The sample in 2 mL of hexane was added to the top of column, and PAHs were eluted with 20 mL of DCM. The solvent was exchanged into hexane, and the final sample volume was adjusted to 1 mL by nitrogen blow-down (*18*).

Samples were analyzed for 14 PAHs (acenaphthene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2-*cd*]pyrene, and benzo[*g,h,i*]perylene) using a HP Model 5890 Series II gas chromatograph and a HP Model 5971A mass selective detector (MSD). An HP-5 column (60 m × 0.32 mm i.d., Hewlett-Packard Corp.) was used. The MSD was operated in selected ion monitoring (SIM) mode. Instrument operating conditions and the ions used for PAH identification and quantification are detailed elsewhere (*14*).

Quality Control. Polyurethane foam (PUF) has been extensively used for SOC air sampling for sample volumes ranging from 300 to 600 m^3. It has been shown by numerous other researchers that breakthrough in these samplers at comparable flow rates and sample volumes is insignificant (*19−22*). In this study in addition to PUF, XAD-2 resin was used. This combination increases adsorption capacity and minimizes post-collection volatilization problems (*23*).

Breakthrough from the WSS resin columns was checked by placing a back-up column into the sampling system during three of the sampling events. In all cases, PAH amounts found in a back-up column were below the limit of detection, indicating that the amount of the resin (~30 g) used in the WSS sorbent column was enough to retain the deposited PAHs.

All samples were spiked with PAHs prior to extraction to determine analytical recovery efficiencies. Recoveries were 64 ± 14% ($n = 128$) for acenaphthene-d_{10}, 74 ± 14% ($n = 131$) for phenanthrene-d_{10}, 79 ± 12% ($n = 131$) for chrysene-d_{12}, and 67 ± 13% ($n = 131$) for perylene-d_{12} for all sample matrixes. Recoveries of the following were used to correct the amounts of specific PAHs found in the samples: acenaphthene-d_{10} for acenaphthene and fluorene; phenanthrene-d_{10} for phenanthrene, anthracene, carbazole, and fluoranthene; chrysene-d_{12} for pyrene, benz[*a*]anthracene, and chrysene; and perylene-d_{12} for benzofluoranthenes, benzo[*a*]pyrene, indeno[1,2-*cd*]pyrene, and benzo[*g,h,i*]perylene.

The amounts found in field blanks were generally less than 10% of the amount in PUFs and WS samples. Blank amounts for PS-1 filters, WSS filters, and plates were 0−47%, 0−13%, and 0−33% of the sample amounts, respectively.

Quantifiable PAH amounts were determined from sequential injections of diluted standard solutions, using a signal-to-noise ratio of 20. This ratio was used because peaks with smaller ratios cannot be reliably integrated (*24*). The quantifiable amounts of PAHs ranged from 0.015 ng (for acenaphthene) to 0.24 ng (for benzo[*g,h,i*]perylene).

The limit of detection (LOD, ng) was defined as the mean blank mass plus three standard deviations (*25−28*). Benz[*a*]anthracene through benzo[*g,h,i*]perylene were not detected (nd) in blanks. LODs for other PAHs ranged from nd to 1016 ng for PS-1 filters, nd to 3970 ng for WSS filters, nd to 2013 ng for PUFs, nd to 6988 ng for WSS resin column, and nd to 1997 ng for dry deposition plates. The largest amounts found in the blanks were for phenanthrene. In general, PAH amounts in the samples were substantially higher than LODs. Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

The analytical method used was tested by analyzing three aliquots of NIST Standard Urban Dust Reference Material (SRM-1649). Concentrations of PAHs found in the SRM-1649, as the percent of NIST certified values, were benz[*a*]anthracene 96%, benzo[*a*]pyrene 88%, benzo[*g,h,i*]perylene 96%, fluoranthene 106%, and indeno[1,2-*cd*]pyrene 117%.

Results and Discussion

Ambient Concentrations. Concentrations of PAHs are reported in two different ways: total PAH concentration and Σ_{14}-PAHs. The total PAH concentration refers to sum of the particulate and gas-phase concentrations of an individual compound, while Σ_{14}-PAHs refers to sum of the concentrations of the 14 measured compounds.

Σ_{14}-PAHs (gas + particulate) ranged from 159 to 863 ng/m^3 with an average of 428 ng/m^3 (*29*). These values are similar to ΣPAHs measured by others even though the total number of PAHs measured varied from study to study. For example in Chicago, IL ΣPAHs was 644 ng/m^3 (Σ_{20}-PAHs) (*30*), 442 ng/m^3 (Σ_{13}-PAHs) (*27*), 150 ng/m^3 (Σ_{11}-PAHs) (*7*), 48−550 ng/m^3 (Σ_{19}-PAHs) (*31*), in Boston, MA 194 ng/m^3 (Σ_{18}-PAHs) and, in Houston, TX 119 ng/m^3 (Σ_{18}-PAHs) (*32*). This similarity is due, in part, to the fact that ΣPAHs was dominated by phenanthrene followed by acenaphthene and fluorene which accounted for 46%, 18%, and 17% of ΣPAHs, respectively (Figure 2). These percentages were very similar to the ones reported by Halsall et al. (*25*) and Cotham and Bidleman (*27*).

In this study, gas and particulate phase Σ_{14}-PAH concentrations ranged from 144 to 853 and 10−48 ng/m^3, respectively. Gas-phase Σ_{14}-PAHs accounted for ~91% of the total ambient concentration. By comparison, Simcik et al. (*31*) measured a range of 27−430 ng/m^3 for gas-phase ΣPAHs

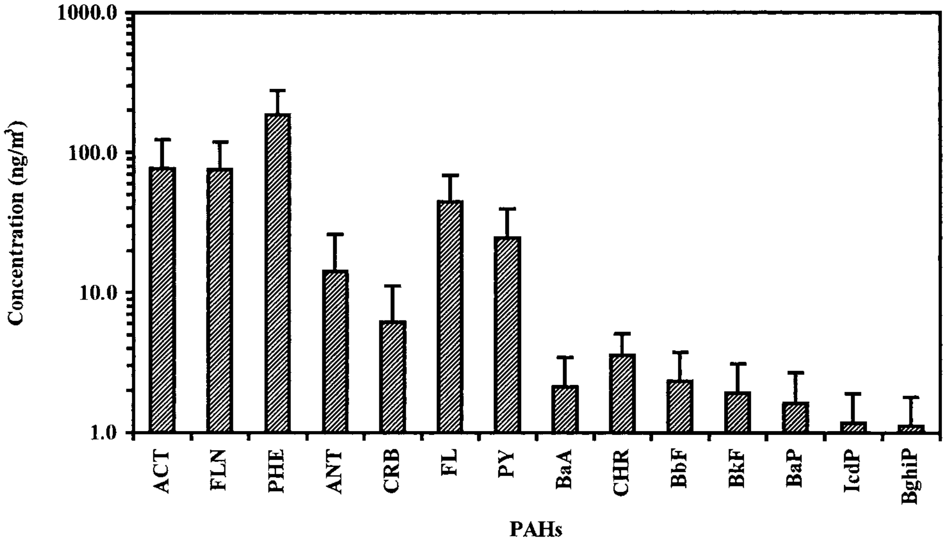

FIGURE 2. Average total (particulate + gas) air concentrations of individual PAHs measured between June and October 1995 in Chicago, IL ($n = 12$). Error bars represent one standard deviation.

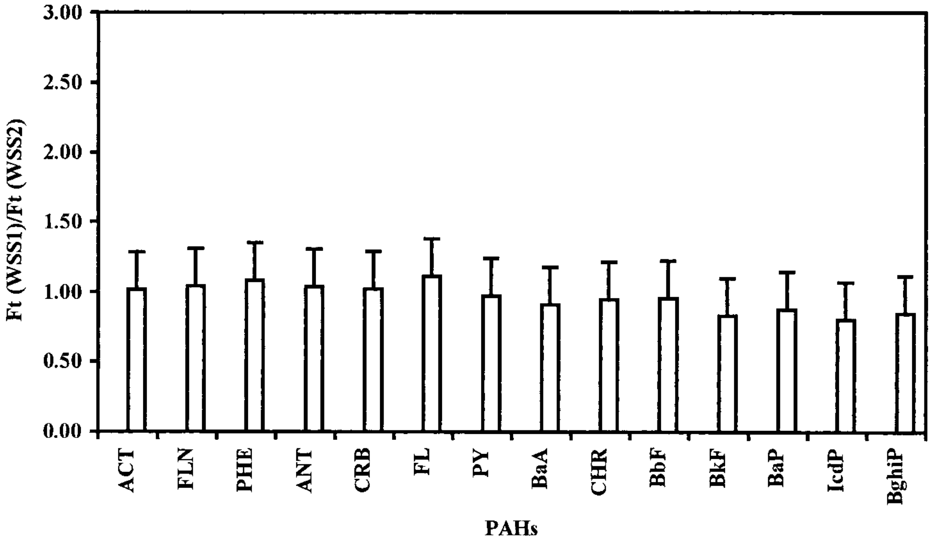

FIGURE 3. Comparison of the total fluxes (F_t) measured by WSS1 and WSS2 ($n = 12$). Error bars represent one standard deviation.

accounting for approximately 90% of the total ambient concentrations, at the same site in Chicago in 1994.

The particle/gas-phase distribution varied widely. The gas-phase percentage generally decreased with increasing molecular weight and ranged from 1.1 to 99.4%. Three-ring PAH compounds (acenaphthene, fluorene, phenanthrene, and anthracene) were associated primarily with the gas phase, while six-ring PAH compounds (indeno[1,2-*cd*]pyrene, benzo[*g*,*h*,*i*]perylene) were associated primarily with the particulate phase. These results were generally consistent with the particle/gas-phase distributions reported in previous studies (*4*, *32*−*34*).

Total (Particle + Gas) Fluxes. The average total PAH flux ratios measured with two water surface samplers, one containing a filter and resin column (WSS1) and one containing only a resin column (WSS2), were close to one (Figure 3). The correlation between the total fluxes measured with WSS1 and WSS2 was very good ($n = 147$, $r^2 = 0.92$, slope = 0.96). Comparison by compound (paired *t*-test, 95% confidence level) indicated that statistically there was not a significant difference between the means of the total fluxes measured with the two samplers. Σ_{14}-PAH fluxes ranged from 172 to 626 μg/m^2 d with an average of 360 ± 146 μg/m^2 d (Table 1). Phenanthrene, fluoranthene, pyrene, and fluorene accounted for 34%, 14%, 10%, and 10% of Σ_{14}-PAH fluxes measured with the WSS, respectively.

Particulate Fluxes. The range for particulate Σ_{14}-PAH flux measured with the dry deposition plates was 27.4−229 μg/m^2 d (average 144 ± 60 μg/m^2 d). Particulate Σ_{14}-PAH fluxes were dominated by phenanthrene, fluoranthene, and pyrene (Table 1). These compounds accounted for 29%, 16%, and 14% of particle phase Σ_{14}-PAH fluxes, respectively. As an overall average, the particulate phase accounted for 39% of the Σ_{14}-PAH flux, while it accounted for only 9% of total air concentration. This difference is due to different deposition characteristics of particles and gases.

In general, the dry deposition fluxes measured in this study were significantly higher than the fluxes reported in other studies because most previous studies involved nonurban areas (Table 1). The particulate Σ_{14}-PAH flux for a residential area in Taiwan was reported as 60.9 μg/m^2 d by Sheu et al. (*35*). A range of 3.4−140 μg/m^2 d for particulate ΣPAH flux was measured in Chicago, IL recently (*36*). These fluxes were comparable to the ones measured during this study.

One of the objectives of this study was to compare the deposition collected by the filter in the water recirculation line, which should remove the particles deposited to the WSS,

TABLE 1. Dry Deposition and Gas Exchange Fluxes[k] of PAHs (μg/m^2 day) Previously Reported

	particle										gas			
PAH[l]	this study	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	this study	*h*	*e*	*j*
ACT	3.3 ± 1.3	6.4	1.6	0.12	0.012						23.5 ± 11.1			−0.493
FLN	4.2 ± 1.7	4.1	2.1	0.11	0.005			0.006	9×10^{-5}	3×10^{-6}	32.2 ± 14	−0.034		0.175
PHE	47.1 ± 18	10.1	2.8	1.56	0.060	0.079	0.16	0.033			73.7 ± 50.9		−0.076	0.132
ANT	1.6 ± 0.8	2.8	3.3	0.19	0.008	0.005	0.16	0.003			7.7 ± 5.2		−0.005	−0.013
CRB	1.9 ± 0.95										6.3 ± 4.0			
FL	25.5 ± 16.6	14.5	2.0	2.71	0.106	0.090		0.044	0.005	2×10^{-4}	29.2 ± 13.2	−0.062	−0.066	−0.822
PY	22.9 ± 13.2	24.3	3.9	2.24	0.077	0.075	0.28	0.041	0.001	1×10^{-4}	17.7 ± 7.6	0.149	−0.062	−0.079
BaA	7.0 ± 4.6	27.7	4.1	1.09	0.025	0.018	0.14	0.016	0.004	2×10^{-4}			−0.011	−0.015
CHR	9.1 ± 5.6	13.0	2.1	1.88	0.094	0.057		0.033	0.017	0.001		0.166	−0.030	−0.085
BbF	9.6 ± 5.8	22.3	9.4	2.91^{m}	0.114^{m}			0.041						0.002
BkF	8.6 ± 5.2	140.0	6.0					0.022						
BaP	7.7 ± 5.0	311.0	7.2	1.10	0.049	0.019	0.26	0.011	0.043	7×10^{-4}		−0.223	−0.010	0.003
IcdP	6.3 ± 4.4	234.0	8.9	0.77	0.031	0.053		0.027	0.056	0.003			0	
BghiP	5.4 ± 3.8	206.0	7.5	0.99	0.048	0.027		0.030	0.045	0.003			0	0.002

[a] Measured with greased dry deposition plates, (*35*) (traffic intersection). [b] Measured with greased dry deposition plates, (*35*) (residential area). [c] Measured with greased dry deposition plates, geometric means (*36*) (Chicago). [d] Measured with greased dry deposition plates, geometric means (*36*) (Lake Michigan). [e] Determined using a mass balance approach (*4*) (Lake Siskiwit). [f] Calculated using a dry deposition velocity of 0.3 cm/s (*37*) (Lake Superior). [g] Calculated using a dry deposition velocity of 0.49 cm/s (*15*) (Chesapeake Bay). [h] Calculated using a hybrid-receptor deposition modeling approach. Particles were assumed to have a mass median diameter of 1.6 μm (*7*) (Lake Michigan). [i] Calculated using a dry deposition velocity of 0.2 cm/s (*38*) (Lake Michigan). [j] Calculated by applying the two-film model to paired water and air concentrations (*39*) (Chesapeake Bay). [k] Negative values imply volatilization of PAHs from water. [l] Acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*c,d*]pyrene (IcdP), benzo[*g,h,i*]perylene (BghiP). [m] Bbf + BkF.

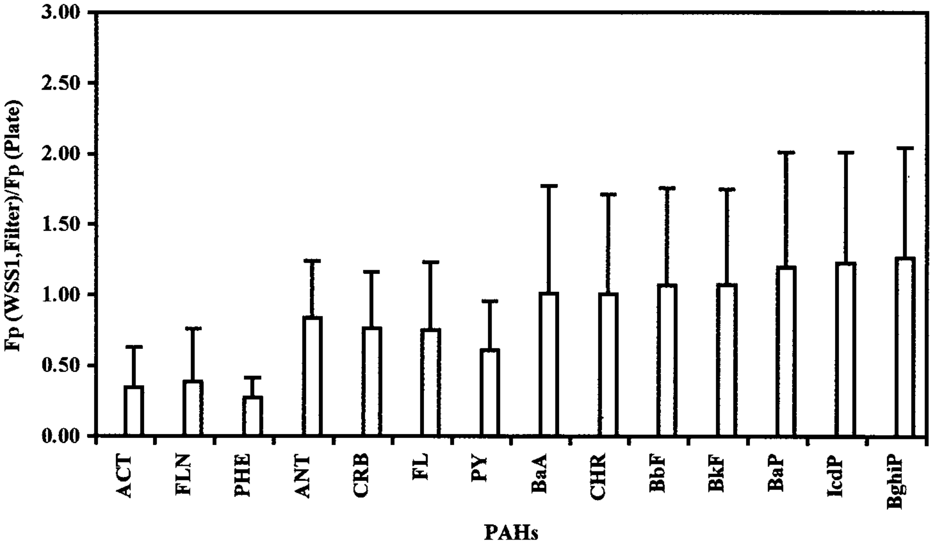

FIGURE 4. Comparison of the particulate fluxes (F_p) measured by WSS1 filter and dry deposition plates. Error bars represent one standard deviation.

with the deposition collected by the deposition plate. For the compounds anthracene through benzo[*g,h,i*]perylene (excluding pyrene) average particulate fluxes measured with dry deposition plates and WSS1 filter (Figure 4) were not statistically different (paired *t*-test, 95% confidence level). However, the fluxes were statistically different for acenaphthene, fluorene, phenanthrene and pyrene. For acenaphthene, fluorene and phenanthrene the particulate fluxes measured with WSS1 filter were approximately two times lower than the fluxes measured with plates.

The difference between the particulate fluxes for some PAHs measured with the WSS and dry deposition plates may be due to the sampling artifacts associated with these two samplers. These artifacts are discussed below.

1. Loss of particulate PAHs on the filter due to dissolution into the water. Since acenaphthene, fluorene, and phenanthrene have higher solubilities than the other compounds, it is probable that the difference between the particulate fluxes measured with plates and WSS1 filter for these compounds is due to the dissolution from particles into the water circulated through the filter during sampling.

2. Losses of particulate PAHs from the deposition plate by evaporation. Myrczik (*40*) compared the PCB fluxes measured with long term (5 days) and combined short term (5 × 1 day) dry deposition samples. Since the samples were collected during summer when temperature was high, evaporation losses were expected to be at a maximum. Although slightly lower fluxes were measured with the long term samples, the values were not statistically different from the short term samples. Therefore, evaporation losses from particles deposited on the plates are probably not very significant. This finding is supported be the results reported here since WWS1 filter fluxes for acenaphthene, fluorene, phenanthrene, and pyrene were less than deposition plate fluxes.

3. Absorption of gas-phase PAHs by the grease used on the plates. It has been suggested that greased surfaces used to measure particle phase dry deposition also capture gas-

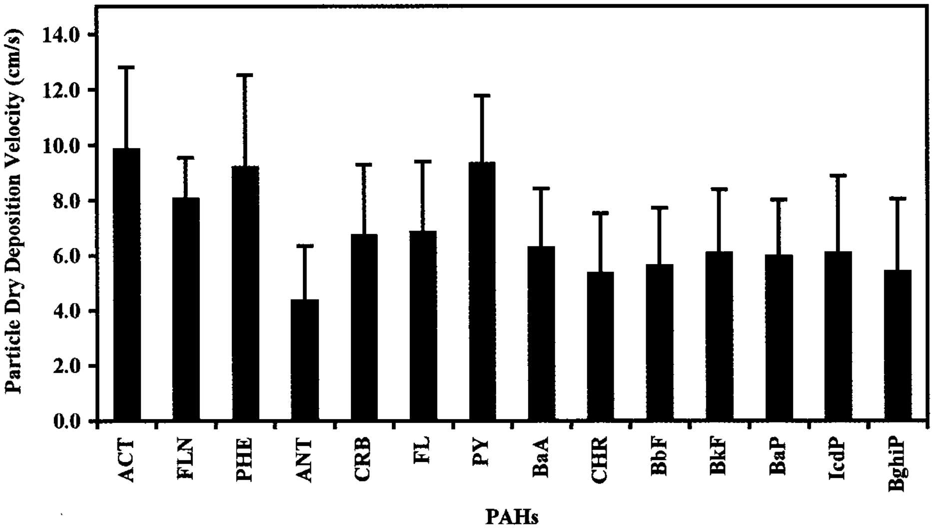

FIGURE 5. Particle phase overall dry deposition velocities. Error bars represent one standard deviation.

phase SOCs (*4, 12, 41–43*). Absorption of gas-phase compounds by grease would increase the fluxes measured with plates and cause them to be higher than those measured with the WSS1 filter. Harner and Mackay (*44*) suggested that octanol–air partition coefficient (K_{OA}) is the single physical-chemical parameter which best describes the partitioning of SOCs among air, soil, and vegetation. K_{OA} may also reflect equilibrium partitioning between air and an organic matrix like the grease used on the deposition plates. The octanol–air partition coefficient, K_{OA}, is defined as

$$K_{OA} = C_O/C_A \qquad (2)$$

where C_O and C_A are the concentrations of the SOC in octanol and air, respectively. K_{OA} can be calculated from the octanol–water partition coefficient and dimensionless Henry's law constant. K_{OA} values were adjusted for temperature by log $K_{OA} = A + B/T$ where A and B were obtained from Harner and Bidleman (*45*).

If octanol is an appropriate surrogate for the grease used on dry deposition plates, equilibrium concentrations of PAHs in the grease can be approximated using octanol-air partition coefficients and the measured gas-phase air concentrations. K_{OA} values for fluorene, phenanthrene, anthracene, and pyrene (at 25 °C) are 7.1×10^6, 4.3×10^7, 1.7×10^7, and 7.41×10^8, respectively (*18*). These values suggest that under equilibrium conditions, compounds with higher molecular weights can be absorbed by the grease in greater quantities than the lower molecular weight compounds.

Assuming equilibrium conditions, quantities absorbed by grease were estimated using temperature adjusted K_{OA} values, the average amount of grease used (1.4 mg/strip), and the measured gas-phase ambient concentrations during each sampling period. These estimated values were compared to the quantities found on the dry deposition plates. Estimated contributions of gas-phase absorption were 3.9%, 5.1%, 6.2%, and 37% for fluorene, phenanthrene, anthracene, and pyrene, respectively. If partitioning is not at equilibrium, these calculated contributions would be overestimated.

Li (*46*) investigated the absorption of gas-phase PAHs by the greased surface of dry deposition plates. This study was performed by exposing the greased plates to gas-phase PAHs under laminar flow conditions for periods ranging from 12 to 400 h. Continuously increasing concentrations in the grease indicated that PAHs did not reach equilibrium for even exposures of 400 h. Sampling durations used in that study were approximately five times higher than the ones used in this study. Therefore, the calculated contributions of gas-phase deposition to the greased surface using the K_{OA} approach are probably overestimated.

In summary it is likely that the differences between fluxes measured with the WSS1 filter and the deposition plate for acenaphthene, fluorene, phenanthrene, and pyrene was due to dissolution from the particles collected on the filter into the water. The difference for pyrene was not as pronounced as it was for acenaphthene, fluorene, and phenanthrene probably because pyrene is less soluble than these compounds. Since the estimated gas-phase absorption by the grease is higher for pyrene (~37%) than other compounds, it is also possible that absorption of gas-phase pyrene by the greased strips contributed to the higher deposition fluxes measured with the deposition plates than those measured with the WSS1 filter.

For benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, and benzo[*g,h,i*]perylene, which are present primarily in particulate phase, mean fluxes measured with dry deposition plate and both WSS1 and WSS2 were not statistically different (paired *t*-test, 95% confidence level), indicating that the majority of the flux of these compounds is due to particle deposition. In addition this finding suggests that the dry deposition plates and the WSS have similar deposition characteristics for atmospheric particles. This hypothesis is supported by other studies with the WSS. Tasdemir (*43*) compared the fluxes measured with WSS1 filter and the plates and reported similar findings for PCBs. Yi et al. (*42*) also reported that dry deposition plates, and the WSS have similar deposition characteristics for atmospheric particles based on the comparison of atmospheric particulate lead and calcium fluxes.

Gas Fluxes. Gas-phase dry deposition fluxes were calculated by subtracting the particulate phase fluxes measured with dry deposition plate from the total (particulate + gas) fluxes measured with the WSS1 and WSS2. Gas-phase fluxes were reported only for the compounds acenaphthene through pyrene which accounted for 99.3% of ambient gas-phase Σ_{14}-PAH concentrations. Gas-phase fluxes were not reported for compounds heavier than pyrene because calculation of gas fluxes for these PAHs requires the subtraction of two nearly equal flux values so that even small differences between WSS1 and WSS2 result in very different calculated fluxes. On average there was a gas flux for these compounds, however statistically (paired *t*-test, 95% confidence interval), the gas and particulate fluxes were the same.

The gas fluxes reported here represent the maximum possible fluxes due to absorption because PAH concentrations in the water were kept near zero. The range for gas-

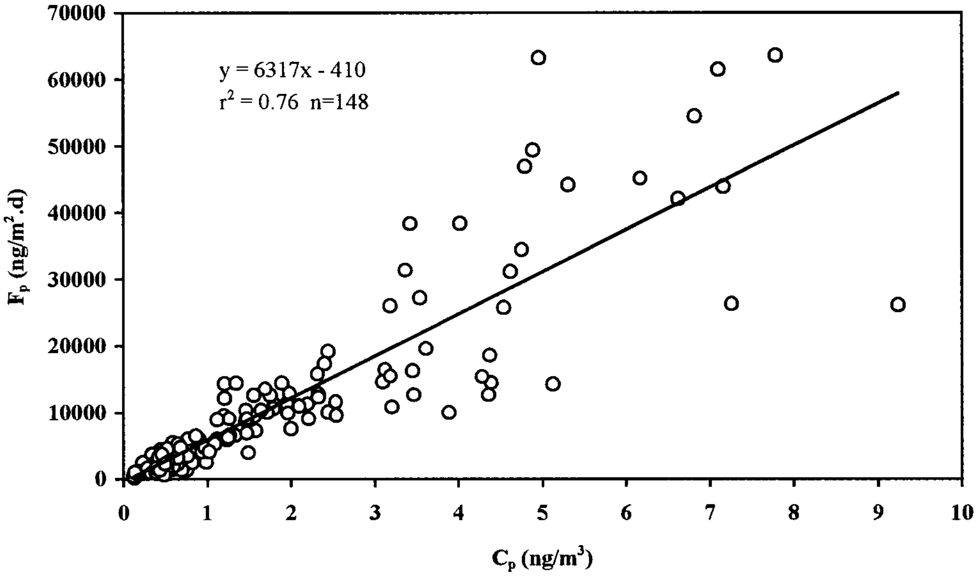

FIGURE 6. Relationship between ambient particulate phase PAH concentrations and particulate PAH fluxes measured with the dry deposition plate.

TABLE 2. Dry Deposition Velocities for Semivolatile Organic Compounds (SOCs) Associated with the Particulate Phase

compd	V_p (cm/s)	comment	ref
PCB	0.50	estimated for submicron particles at 14 m/s wind speed using the model by Sehmel and Sutter	(*52*)
PAH	0.99	calculated by a mass balance model	(*4*)
SOC	0.20	estimated using the model by Slinn and Slinn for small (0.5 μm) and large (5 μm) particles assuming a small-to-large ratio of 1.5:1	(*2*)
PAH	0.67−1.8[a]	dry deposition plates	(*32*)
PCB	5.00	dry deposition plates	(*8*)
PCB	6.5 ± 5.0	dry deposition plates	(*43*)
PCB	4.4−7.2	dry deposition plates	(*36*)
PAH	0.4−3.7	dry deposition plates	(*36*)
PAH	4.5 ± 3.1	dry deposition plates	(*53*)
PAH	6.7 ± 2.8	dry deposition plates	this study

[a] V_p was calculated by dividing the flux measured with dry deposition plate by total (particulate + gas) air concentration.

phase Σ_7-PAH flux was 69−263 μg/m^2 d (average 170 ± 72 μg/m^2 d). Gas-phase Σ_7-PAH fluxes were dominated by phenanthrene, fluoranthene, and pyrene (Table 1). As an overall average, the gas phase accounted for ~61% of the Σ_{14}-PAH flux, while it accounted for ~91% of total air concentration.

Reported gas-phase fluxes for lakes estimated using the two-film model range from 0.002 μg/m^2 day to 1.32 μg/m^2 day for different compounds (Table 1). The direction of individual gas-phase fluxes (volatilization or absorption) varies at different locations depending on their fugacity difference between air and surface water. Previously reported values are much lower than the fluxes measured in Chicago, IL with the WSS probably due to significantly lower atmospheric concentrations over the lakes and different water concentrations.

Particulate Phase Overall Dry Deposition Velocities. Figure 5 shows the particulate phase overall dry deposition velocities for PAHs calculated by dividing the particulate fluxes measured with dry deposition plates by ambient particulate concentrations (eq 1). They range from 4.3 to 9.8 cm/s with an overall average of 6.7 ± 2.8 cm/s. The average overall particle phase dry deposition velocity for PAHs with molecular weights between 154 and 202 was 7.7 cm/s, and for PAHs with molecular weights between 228 and 276 it was 5.8 cm/s. This decrease in deposition velocity with increasing molecular weight is supported by other experimental studies which have shown that a greater fraction of the higher molecular weight PAHs are associated with fine particles relative to the lower molecular weight compounds (*23, 32, 48, 49*).

Figure 6 shows a good correlation ($r^2 = 0.76$) between the particulate phase PAH fluxes and ambient particulate concentrations. The slope of the linear regression line (6300 m/d or 7.3 cm/s) is the apparent best-fit particulate overall dry deposition velocity which agrees well with the average value of 6.7 cm/s reported above.

The dry deposition velocity of anthracene was the lowest among the measured PAHs and about half of that calculated for phenanthrene (9.2 cm/s). Although their molecular weight is the same, reactivities of phenanthrene and anthracene are different. According to the reactivity scale developed by Nielsen (*50*) anthracene is one of the most reactive PAHs measured in this study. Reactive losses of anthracene in the atmosphere and in simulated atmospheres have been previously observed (*26, 51*).

In this study the average phenanthrene/anthracene (stable/reactive) ratio for particulate air concentrations was 17.1, while the average flux ratio was 40.6. Concentration ratios obtained from different samples were well correlated with flux ratios ($r^2 = 0.80$). It is therefore possible that the low anthracene fluxes (and subsequently low deposition velocities) were due to its loss from the dry deposition plate during exposure to solar radiation and atmospheric oxidants during sampling.

Reported values for the particle phase dry deposition velocities of semivolatile organic compounds are summarized in Table 2. The ratio between the dry deposition velocities calculated in this study and previously reported values vary between 1.03 and 33.5. It should be noted that some of the values are not directly comparable to the results of this study because of differences in experimental procedures, estimation techniques employed, and physical properties of the compounds.

The agreement between the calculated dry deposition velocities in this study and the reported values using similar techniques is good (*8, 43, 53*). The values reported by Sheu et al. (*35*) were lower than the dry deposition velocities calculated in this study although the sampling procedures were similar probably because they calculated dry deposition velocities using the measured dry deposition fluxes and total (particulate + gas) ambient concentrations, assuming that the dry deposition plate collects both gas and particulate dry deposition. Based on the analysis of gas-phase deposition to the greased surfaces discussed above (which indicated little sorption), this would result in an underestimation of particle associated PAH dry deposition velocities.

The discrepancy between the experimental and estimated dry deposition velocities may be due to large particles (>10 μm) which were not taken into consideration in the dry deposition velocity estimates by Hoff et al. (*2*) and Doskey and Andren (*52*). However, results of the study by Holsen et al. (*8*) indicated that the contribution of coarse particles to the dry deposition fluxes of PCBs was important. Lipiatou et al. (*54*) also reported that the dry deposition fluxes of PAHs were dominated by the coarse particles (about 50−90%) in the western Mediterranean Sea.

The presence of PAHs on coarse particles has been previously reported (*24, 33, 48, 49*). However, the maximum cut diameter of the instruments used in those studies was 20 μm, and they did not provide information about the quantity of PAHs existing on larger particles (>20 μm). The PS-1 sampler collects particles with diameters smaller than approximately 25 μm (*2*), and the cut diameter varies depending on the orientation of the sampler with respect to the direction and speed of the wind (*55*). If there is a considerable amount of PAHs on the particles larger than 25 μm, the calculated deposition velocity will be inflated because the air concentration is underestimated. This inflation would be more important for lower molecular weight PAHs since they are associated with coarse particles to a greater extent than higher molecular weight compounds (*24, 33, 48, 49*).

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